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X-Ray Photoelectron Spectroscopy of Some Nickel Compounds

By L. O. Pont, A. R. Siedle,[1] M. S. Lazarus, and W. L. Jolly*

We have determined the nickel $2p_{3/2}$ binding energies of various nickel complexes, including dicarbollide complexes in which the nickel ostensibly has oxidation states of +3 and +4. The data are presented in Table I. We note two significant features of the data.

First, the binding energies of the Ni(III) and Ni(IV) dicarbollide complexes are of the same general magnitude as those of the Ni(II) complexes. This is at first sight surprising because of the expected correlation of binding energy with oxidation state. (Thus, Tolman et al.[2] have observed that the Ni $2p_{3/2}$ binding energy for K_2NiF_6 is about 5 eV higher than the average value found for typical Ni(II) compounds.) We believe the low binding energies of the dicarbollide complexes are a consequence of the low electronegativities of the donor atoms in these complexes. The nickel-coordinated carbon and boron atoms of the dicarbollide groups donate considerably more electron density to the metal atoms than do the relatively electronegative oxygen and nitrogen atoms in complexes such as $Ni(H_2O)_6^{2+}$ and $Ni(en)_3^{2+}$. Consequently, the atomic charges of the nickel atoms in the two classes of complexes are not markedly different. The

Table I

Nickel $2p_{3/2}$ Binding Energies

Compound	Ni Oxid. State	E_B, eV
$(1,2\text{-}B_9C_2H_{11})_2Ni$[a]	4	857.2
$[1,2\text{-}(CH_3)_2B_9C_2H_9]_2Ni$[a]	4	856.6
$(B_{10}H_{10}CNH_3)_2Ni$[b]	4	856.5
$Rb[(1,7\text{-}B_9C_2H_{11})_2Ni]$[c]	3	855.9
$K[(1,2\text{-}B_9C_2H_{11})_2Ni]$[a]	3	855.6
$K\{[1,2\text{-}(CH_3)_2B_9C_2H_9]_2Ni\}$[a]	3	855.6
$[Ni(H_2O)_6]Cl_2$	2	857.7
$K_2[Ni(CN)_4]\cdot H_2O$[d]	2	856.6
$K[Ni(gly)_3]$[e,f]	2	856.5
$KNiIO_6\cdot 0.5H_2O$[g]	2	856.0
$Ni(DMG)_2$[h]	2	855.6
$[Ni(en)_3]S_2O_3$[i]	2	855.6
$(C_5H_5)_3Ni_3(CO)_2$[j]	1	855.0

[a] L. F. Warren, Jr., and M. F. Hawthorne, J. Amer. Chem. Soc., 92, 1157 (1970). [b] W. H. Knoth, J. Amer. Chem. Soc., 89, 3342 (1967). [c] M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe and P. A. Wegner, J. Amer. Chem. Soc., 90, 862 (1968). [d] W. C. Fernelius and J. J. Burbage, Inorg. Syntheses, 2, 227 (1946). [e] gly = glycinate. [f] J. Hidaka and Y. Shimura, Bull. Chem. Soc. Jap., 43, 2999 (1970). [g] Ref. 4. [h] DMG = dimethylglyoximate. [i] N. F. Curtis, J. Chem. Soc., 3147 (1961). [j] E. O. Fischer and C. Palm, Chem. Ber., 91, 1725 (1958).

data serve to emphasize the fact that there is no direct correlation between the oxidation state and charge of an atom.

Second, there is a definite increase of about 1 eV in binding energy on going from the Ni(III) dicarbollide complexes to the Ni(IV) dicarbollide complexes. Apparently the increase in positive charge accompanying one-electron oxidation is somewhat localized on the nickel atoms, and there is no need to consider redox reactions of the ligands. This result is in contrast to that obtained for nickel dithiolate complexes.[3] Redox reactions of the latter complexes involve no significant Ni $2p_{3/2}$ shifts, indicating that the valence electrons are principally added to or removed from the ligands.

Several other points are worthy of mention. We have no good explanation for the low binding energy observed for $KNiIO_6 \cdot 0.5H_2O$, which is supposed to be a Ni(IV) complex.[4] Perhaps our data correspond to a thin layer of reduction product on the surface of the sample. Or perhaps the compound is really a Ni(II) complex with coordinated peroxo groups; samples of this compound invariably show a weak paramagnetism. The fairly high binding energy observed for the Ni(II) complex $K_2[Ni(CN)_4] \cdot H_2O$ (in spite of the coordination of relatively electropositive carbon atoms) is probably attributable to back-bonding. The low binding energy observed for $(C_5H_5)_3Ni_3(CO)_2$ is consistent with the low oxidation state of nickel and the low electronegativity of the coordinated carbon atoms.

Experimental Section[5]

Aluminum K_α X-rays were used with the iron-free, double-focussing magnetic spectrometer.[6] The compounds were either purchased or prepared by procedures given in the references indicated in Table I. Each compound was powdered and brushed onto two copper tapes which were mounted on separate metal sample holders. One sample was coated with a thin layer (2×10^{-4} mg/cm^2) of gold by vacuum deposition. The chemical shift between the nickel $2p_{3/2}$ level and a core level of some other element in the compound which served as an intermediate reference (e.g., boron, chlorine, etc.) was determined from the spectrum of the uncoated sample. The chemical shift between the core level of the reference element and the $4f_{7/2}$ level of gold was determined from the spectrum of the gold-coated sample. The two data were then used to calculate the binding energy of the nickel $2p_{3/2}$ level, assuming a binding energy of 84.0 eV for the gold $4f_{7/2}$ level.[7] This roundabout procedure was necessitated by the extremely weak Ni $2p_{3/2}$ peaks observed for gold-coated samples. The full width at half maximum for the Ni $2p_{3/2}$ peaks was generally about 3 eV; duplicate runs indicated that the chemical shifts are reproducible to ±0.3 eV.

We were unable to obtain a satisfactory spectrum of the Ni(IV) complex $(NH_4)_6NiMo_9O_{32}$; the Ni $2p_{3/2}$ peak was buried in the background noise. The compound turned from black to grey upon X-ray irradiation; undoubtedly decomposition occurred. The measured magnetic susceptibility of the $KNiIO_6 \cdot 0.5H_2O$ sample corresponded to $\mu_{eff} = 0.7$.

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References

(1) U. S. National Bureau of Standards, Washington, D. C. 20234.

(2) C. A. Tolman, W. M. Riggs, W. J. Linn, C. M. King, and R. C. Wendt, Inorg. Chem., 12, 0000 (1973).

(3) S. O. Grim, L. J. Matienzo, and W. E. Swartz, J. Amer. Chem. Soc., 94, 5116 (1972).

(4) P. Ray, Inorg. Syntheses, 5, 201 (1957); P. Ray and B. Sarma, J. Indian Chem. Soc., 25, 205 (1948).

(5) Further experimental details may be found in L. O. Pont, Master's Thesis, University of California, Berkeley, May, 1973, Lawrence Berkeley Laboratory Report LBL-1829.

(6) J. M. Hollander, M. D. Holtz, T. Novakov, and R. L. Graham, Ark. Fys., 28, 375 (1965); T. Yamazaki and J. M. Hollander, Nucl. Phys., 84, 505 (1966).

(7) C. S. Fadley and D. A. Shirley, J. Res. Nat. Bur. Stds., Sect. A, 74, 543 (1969); W. P. Dianis and J. E. Lester, Anal. Chem., 45, 1416 (1973).